PB84-189646

Method for Collection and Analysis of Chlorobenzenes

Monsanto Research Corp., Dayton, OH

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

May 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-189646

EPA-600/3-84-058
May 1984

METHOD FOR COLLECTION AND ANALYSIS OF CHLOROBENZENES

by

G. W. Wooten, J. E. Strobel, R. C. Gable,
J. V. Pustinger, and C. R. McMillin
Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio 45407

Contract No. 68-02-3500

Project Officers

B. W. Gay, Jr. and J. D. Mulik
Atmospheric Chemistry and Physics Division
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-84-058		PB84 189646

4. TITLE AND SUBTITLE	5. REPORT DATE
METHOD FOR COLLECTION AND ANALYSIS OF CHLOROBENZENES	May 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Wooten, G. W., J. E. Strobel, R. C. Gable, J. V. Pustinger, and C. R. McMillin	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Monsanto Research Corporation Dayton Laboratory Dayton, Ohio 45407	CCUL1A/02 - 0673 (FY-84)
	11. CONTRACT/GRANT NO.
	Contract # 680-02-3500
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final 9/81-3/83
	14. SPONSORING AGENCY CODE
	EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

To measure ambient concentrations and individual exposure to potentially hazardous chlorinated organic compounds, analytical methodology using absorbent-based samplers (passive exposure devices) and gas chromatographic techniques were developed. The samplers selectively absorb and concentrate chlorinated organics and other organic compounds diffusing into the solid absorbent. Analysis is carried out by desorption of the trapped compounds by heating, separation by gas chromatography and detection using a Hall detector for the chlorinated organics. Sampling and analytical techniques were evaluated under laboratory conditions with low concentrations of gaseous compounds and optimized for detection and quantitation. The samplers and analytical techniques are capable of detecting subparts-per-billion concentrations of test compounds after one-half hour exposure.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	48
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This program addresses the development of atmospheric monitoring techniques for potentially hazardous organic compounds including halogenated hydrocarbons and benzene. To measure individual exposures to these substances, personal monitors and analytical methodology using sorbent-based passive samplers (passive exposure monitors) and gas chromatographic (GC) analytical techniques were developed. The sampling/analytical techniques were evaluated under laboratory conditions with generated vaporous samples of the compounds and optimized for detection and quantitation. The passive dosimeter and analytical technique used for this project has been found to be capable of detecting one-half part-per-billion of the subject compounds after as little as one-half hour of sampling. Passive dosimeter results have correlated well with results obtained on pumped sorbent tubes collected in parallel. The sampling/analytical methods were further validated with field samples, keying on a quantitative analysis of the halogenated hydrocarbons and benzene.

CONTENTS

Abstract iii
Figures vi
Tables vii

1. Introduction 1
2. Sampling and Analysis Procedures for Chlorinated Organics 3
   - Description of the passive dosimeter monitor. . . 4
   - Analytical procedure for solid sorbent sampling tubes and passive dosimeter. 7
3. Experimental 17
   - Experimental test facilities. 17
   - Sorbent selection 22
   - Dosimeter test results. 24
4. Effects of Environmental Factors 25
   - Gas bag experiments with PHI compound 25
   - Gas bag experiments with complex gas mixture. . . 29
   - Solid sorbent studies 32
5. Results and Conclusions 39

FIGURES

Number		Page
1	Steps involved in using passive dosimetry.	4
2	Assembled dosimeter shown in sampling mode	5
3	Passive dosimeter for laboratory prefield testing and evaluation	6
4	Elements of passive dosimeter.	7
5	Dosimeter thermal desorption/trap unit	8
6	Thermal desorption/trap unit schematic	9
7	Heater control unit.	10
8	Repesentative chromatographic program.	12
9	Compound specificity enhancement by use of multiple GC detectors.	13
10	Chromatogram of halogenated hydrocarbon mixture No. 1.	14
11	Chromatogram of halogenated hydrocarbon mixture No. 2.	15
12	Chromatogram of halogenated hydrocarbon mixture No. 3.	16
13	Standard Sample Generation System (SGS) with effluent monitor modification.	18
14	Exposure chamber for dosimeter testing and evaluation	21
15	Environmental test chambers for exposure of monitors to selected gases and vapors.	23

FIGURES (continued)

Number		Page
16	UV light box used for photoexcitation.	26
17	UV-Vis absorption spectrum of Teflon sample bag. .	27
18	Flow diagram for Model 320 modified thermal desorption system	31
19	GC/MS traces of the exhaust gases before and after exposure	36
20	Ozone exposure study	38

TABLES

Number		Page
1	Gas Chromatograph/Hall Electrolytic Conductivity Detector Conditions for Dosimeter Analysis . . .	11
2	Dosimeter Test Results-Single Face One Hour Sampling	24
3	Percent Recovery vs Exposure to UV Radiation . . .	28
4	Percent Recovery on Exposure to Light Box.	28
5	Ozone Exposure Studies	29
6	Unexposed Sample Percent Change in Composition . .	33
7	Percent Change in Composition Upon Exposure to UV Radiation.	33
8	Relative Amounts in the Unexposed Sample	34
9	Compounds Detected by Mass Spectrometry.	35
10	UV Radiation Study of Spiked Sampling Tubes. . . .	37
11	Ozone Exposure of Spiked Sorbent Tubes	37

SECTION 1

INTRODUCTION

The goal of the Public Health Initiative (PHI) is to establish an ongoing human exposure monitoring capability within the EPA. The basic approach of this program is to measure individual exposures to toxic substances through the main exposure pathways of air, drinking water, and food. The ultimate result of the initiative will be a field-tested methodology for measuing human exposure to toxic substances in defined geographical areas.

This program addresses one portion of the PHI program -- the development of atmospheric monitoring techniques for potentially hazardous organic compounds, including chloroform, chlorobenzene, benzene, carbon tetrachloride, 1,1,1-trichloroethane, 1,1-dichloroethane, tetrachloroethylene, and trichloroethylene.

To measure individual exposures to these substances, personal monitors and analytical methodology were developed for these compounds. The sampling/analytical techniques were evaluated under laboratory conditions with generated vaporous samples of the compounds and optimized for detection and quantitatation. A laboratory investigation was conducted on the effects of "environmental factors," such as ultraviolet (UV) light, water, and ozone, on the chemical integrity of the compounds of interest in generated vaporous samples. The sampling/analytical methods were validated with field samples, keying on a quantitative analysis of the halogenated hydrocarbons and benzene.

The tasks involved in this contract can be summarized as follows:

Task 1 - Develop, optimize, and evaluate sampling/analysis procedures in the laboratory and in the field.

Task 2 - Evaluate the effects of environmental factors on sampling/analysis procedures.

Although defined as a task on this contract, Task 1 work was conducted primarily under a similar MRC-EPA contract (No. 68-02-3469), which developed the passive exposure monitor (PEM) as a sampling device for low-concentration hazardous organic compounds including the halogenated and aromatic compounds listed on previous page. The PEMs were evaluated extensively on a lab scale and in addition, ambient air monitoring was conducted to demonstrate sensitivity and specificity of the approach. Work station monitoring demonstrated the dynamic range of the monitoring approach and provided comparisons with data obtained by the activated charcoal sampling tubes. Results of the PEM lab and field studies are presented entirely in the contract final report for EPA No. 68-02-3469.

Description of the PEM sampling unit and the analytical system is provided in this report in Section 2.

The test facilities used to conduct work for Task 2 under this contract is described in Section 3.

Results of tests on the effect of environmental factors on the PEMs is described in Section 4.

SECTION 2

SAMPLING AND ANALYSIS PROCEDURES FOR CHLORINATED ORGANICS

Solid porous polymers have found wide acceptance as means for collecting and concentrating organic compounds in ambient air and other sampling environments. Sorbent-based active (pump-driven) sampling systems as well as passive sampling devices are customarily employed for such assignments where compound concentrations at the part-per-trillion (ppt) to part-per-billion (ppb) levels are encountered. Sampling is on a time-weighted basis, whereby organics of interest are quantitatively collected onto the sorbent bed, recovered by thermal desorption, and subsequently analyzed by standard gas chromatographic (GC) techniques utilizing specific GC detectors.

The first task under this contract was to develop, optimize, and evaluate sampling and analysis procedures for chlorinated organic compounds in ambient air. However, the sampling and analytical concept was developed primarily on contract No. 68-02-3469, entitled "High Performance Passive Dosimeter for Ambient Air and Short-Term Personal Monitoring Applications," resulting in a miniature passive dosimeter containing a solid sorbent. The chlorinated organic vapors diffuse to the solid sorbent in the dosimeter and are thereby concentrated over a period of time. Subsequently, the trapped vapors are removed by thermal desorption and quantitated via gas chromatography (GC) or tandem-coupled gas chromatography/mass spectroscopy (GC/MS). The development work on the minature passive dosimeter has been reported in the final report for contract No. 68-02-3469.

Application of the solid sorbent sampling approach to specific sampling problems involved three principal areas of technology: pump rates and/or diffusion considerations, sorbent selection, and chemical quantitation of the sampled compounds, which intimately involves desorption of the compounds from the sorbent sampling tube or passive device. Figure 1 illustrates schematically the steps involved in using passive dosimetry.

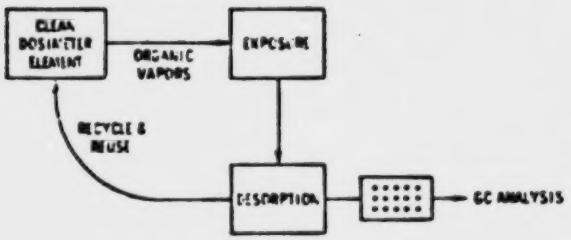


Figure 1. Steps involved in using passive dosimetry.

DESCRIPTION OF THE PASSIVE DOSIMETER MONITOR

The passive dosimeter for personal monitoring of chlorinated organic compounds in ambient air was based upon the following design criteria:

- Rugged, simple design
- Inexpensive, easy operation
- Small size
- High equivalent pump rate
- Multicomponent capability
- Ability to be reused and recharged
- Amenability to thermal desorption

Although laboratory and field performance evaluation studies in this program were conducted using volatile chlorinated organic compounds, the resulting dosimeter design is not limited to this compound class but can be extended to a broad spectrum of compounds through sorbent selection and appropriate analytical procedures.

Unlike commercially available dosimeters, the Monsanto Research Corporation passive dosimeter design shown in Figure 2 is constructed of stainless steel. This material was chosen for three reasons. First, all-metal construction makes the device amenable to thermal desorption which substantially contributes to the high overall detection sensitivity required for ambient sampling. Second, metal construction helps eliminate the possible sinks and/or sources problems for volatile organics associated with some plastic materials. Third, such construction leads to a rugged device that can withstand the rigors of a single sampling assignment and be reused many times, thus leading to a very cost-effective device.

Figure 2. Assembled dosimeter shown in sampling mode.

Basically, the dosimeter (Figures 2 through 4) consists of a stainless steel body, 3.8 cm (1-1/2 in.) in diameter and 1.1 cm (7/16 in.) high. The internal diameter of the body is 3.5 cm (1-3/8 in.) with the exception of the central portion, which is reduced to 3.0 cm (1-3/16 in.) ID to provide a precisely defined containment volume for the porous polymer. Stainless steel screens and perforated plates serve to confine the polymer within the dosimeter body and provide diffusion barriers. A 200-mesh square wire cloth (Cleveland Wire Cloth and Manufacturing Company) with 33.6 percent open area is used for the diffusion screens. Backup plates are punched from stainless steel perforated stock having 0.10-cm (0.040-in.) diameter holes in a straight line center pattern, 34.9 holes/cm^2 (225 holes/$in.^2$) and 28 percent open area. Four screens and perforated plates are used in each dosimeter and arranged in a symmetrical configuration. Dosimeter assembly begins with the placement of a screen and backup plate in the dosimeter, seated on the shoulder of the center body web. A friction snap ring is used to seal the screen and plate tightly against the web shoulder. This describes a volume to contain the solid sorbent. Once a measured amount ($\sim$0.4 g) of sorbent is placed in the dosimeter, a screen and perforated plate are placed over the sorbent and seated on the web shoulder. Additional screen plate retainer rings are added to both faces of the dosimeter to complete the diffusion zone. The dosimeter is easily assembled, and disassembly is simple when the sorbent needs to be replaced or changed. Tenax GC is the solid sorbent selected for this work on the basis of testing described in Section 3.

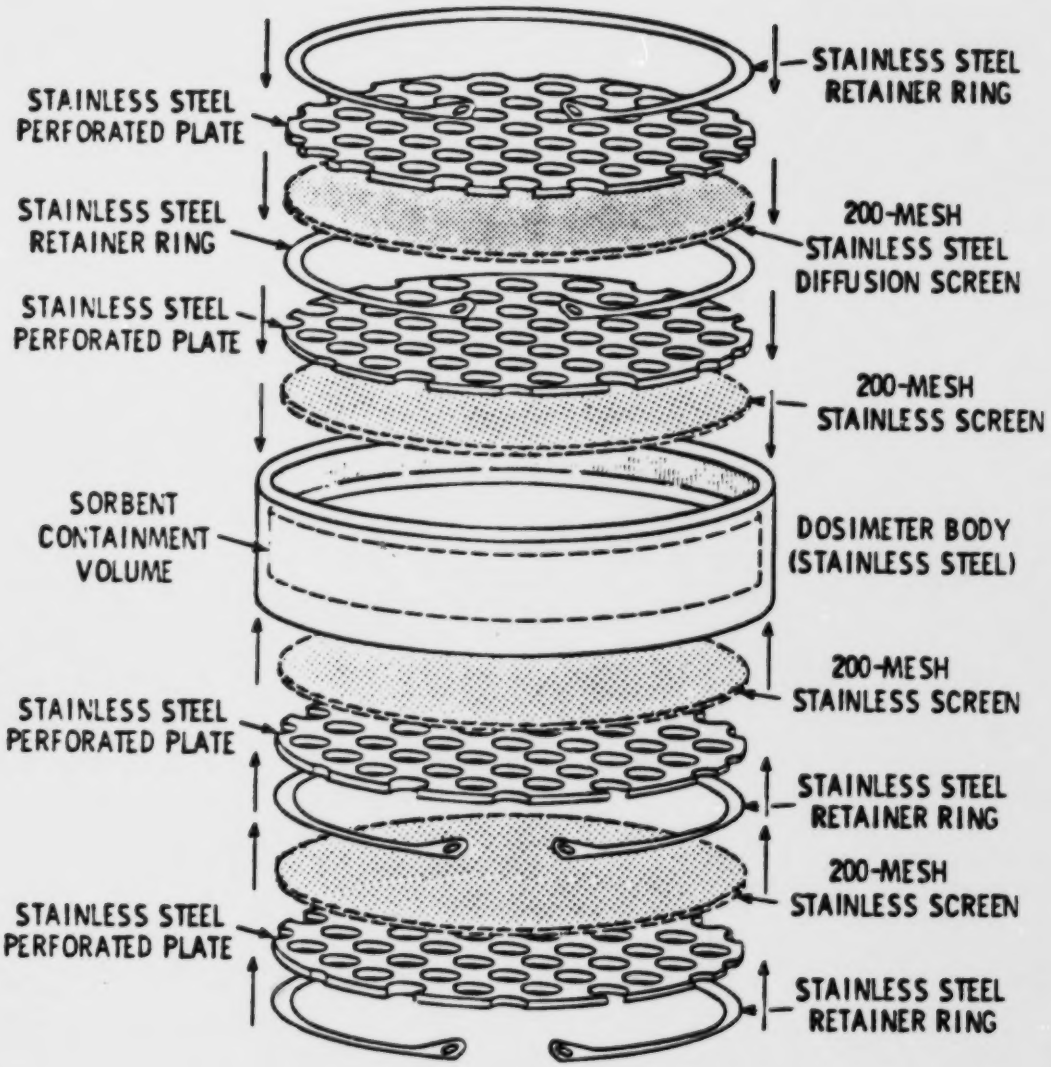


Figure 3. Passive dosimeter for laboratory prefield testing and evaluation.

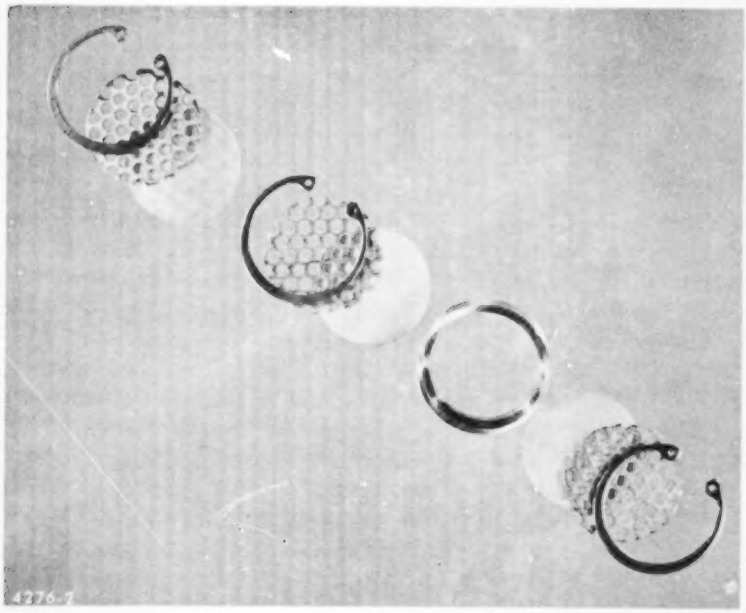
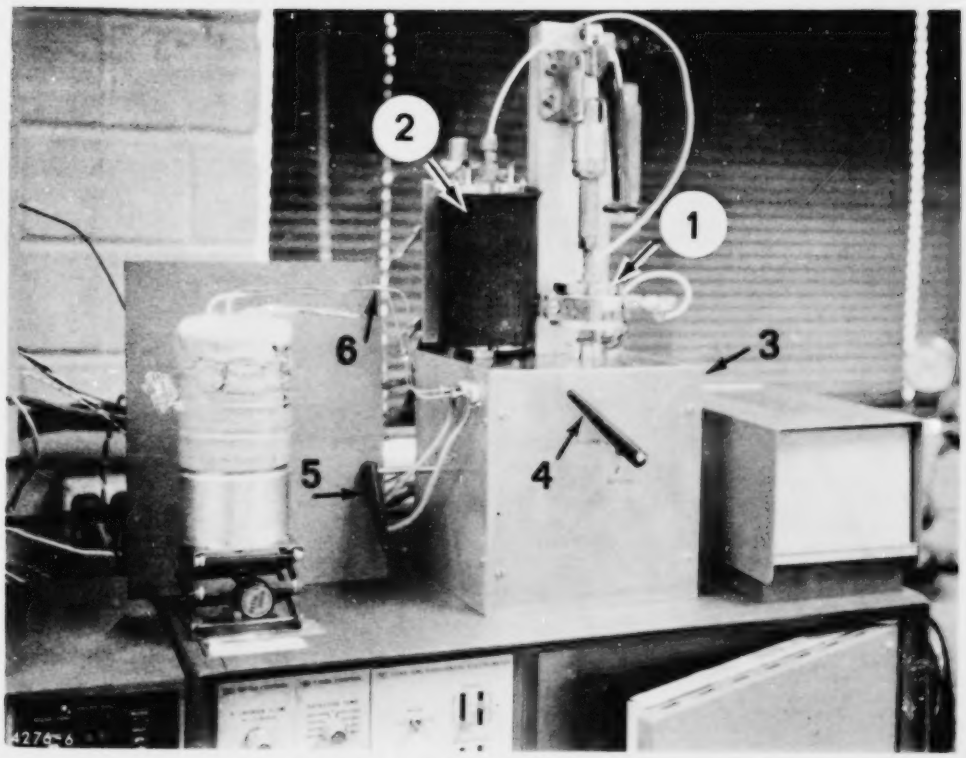


Figure 4. Elements of passive dosimeter.

ANALYTICAL PROCEDURE FOR SOLID SORBENT SAMPLING TUBES AND PASSIVE DOSIMETER

Dosimeter Thermal Desorption/Trap Unit

Thermal desorption capabilities are paramount to ambient air monitoring with passive dosimeters. For this study, the thermal desorption oven required for dosimeter desorption/analysis was designed to ensure reliable performance during this critical operation step and to facilitate handling a large number of dosimeters. The assembly, shown in Figure 5, handles the desorption of sorbent sampling tubes (dynamic flow) as well as the newly designed passive dosimeters. The unit is composed of two manually operated, six-port, high-temperature (300°C max.) Valco® valves. "Switching valve" No. 1 (Figure 6) directs helium purge gas through either the sorbent tube or the passive dosimeter path to a second valve which selects the "desorb/trap" or "analyze" mode of operation. The "desorb/trap" mode diverts the purge gas through a cryogenically cooled sample loop to provide off-line trapping which, in addition, provides better carrier gas flow rate control. When valve No. 2 is switched to the "analyze" mode, a second gas stream (helium carrier-gas) is backflushed through the sample loop, which is now ballistically heated to transfer the trapped compounds to the analytical column for high-resolution chromatographic analysis.



(1) Dosimeter thermal desorption oven

(2) Sorbent sampling tube desorption oven

(3) Insulated valve housing

(4) Desorb-analyze mode valve

(5) Dosimeter-tube selector valve

(6) Ballistically heated trap

Figure 5. Dosimeter thermal desorption/trap unit.

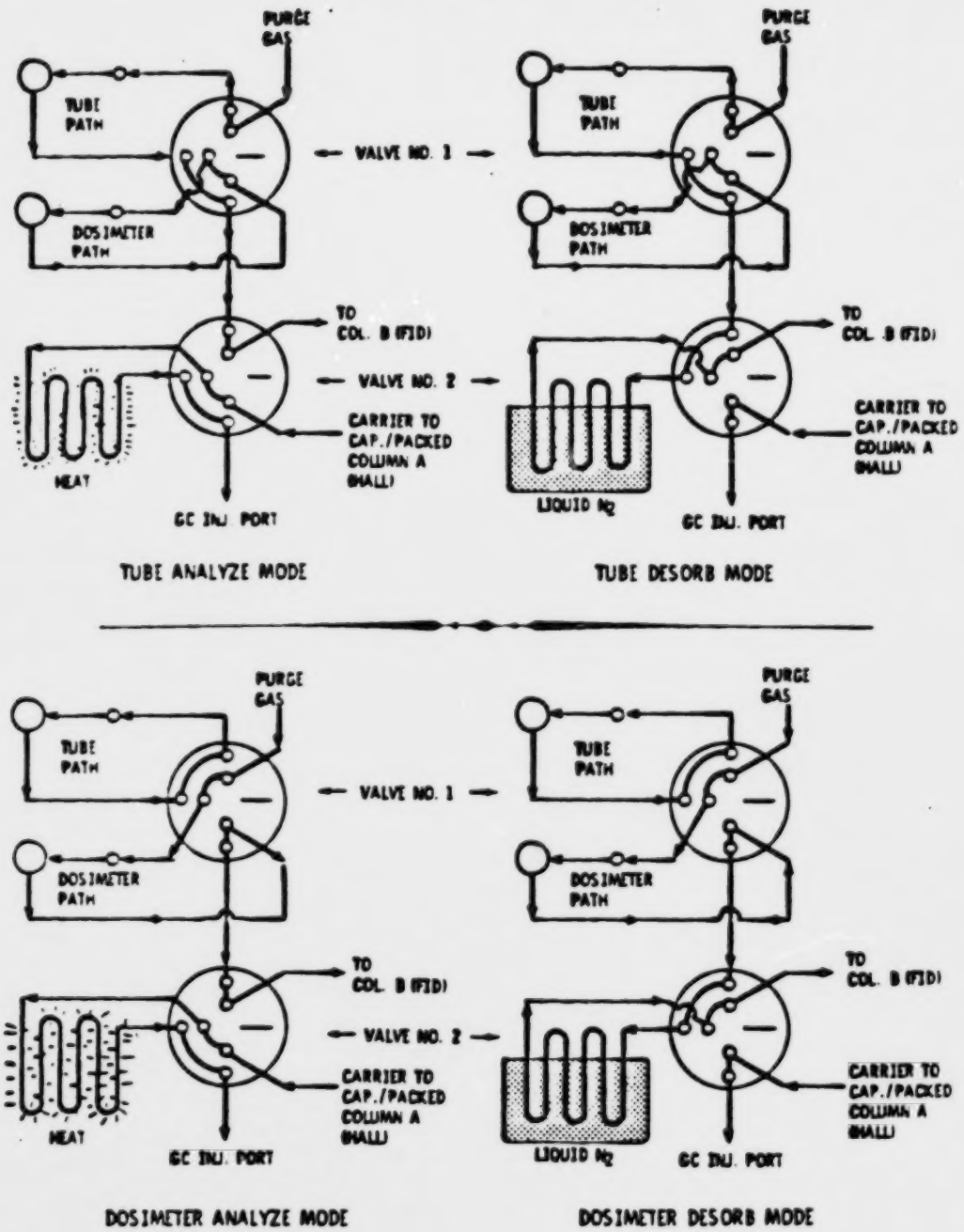


Figure 6. Thermal desorption/trap unit schematic.

The heater control unit shown in Figure 7 provides manual control to five heat zones, two of which can be operated by a timer.

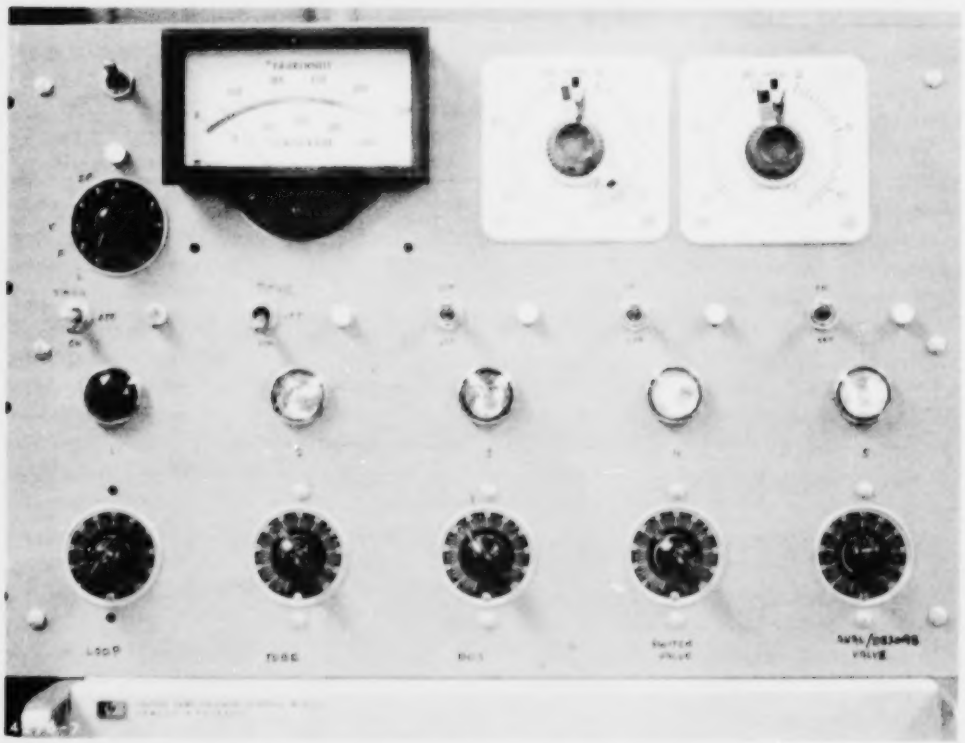


Figure 7. Heater control unit.

Up to eleven thermocouples can be strategically placed to monitor various locations. In our application, the heater control unit sets and monitors the thermal desorption unit as follows:

Position No.	Description
1	Sample loop (time controlled for 10 min)
2	Sorbent tube desorption heater
3	Passive dosimeter desorption heater
4	Switching valve No. 1
5	Analyze/desorb valve No. 2

Chromatographic Program for Sorbent Tube and Dosimeter Analysis

Compound recognition capabilities were included in the chromatographic analytical program to better identify the broad range of chlorinated compounds often collected under field sampling conditions.

Chromatographic conditions employed for the analysis of dosimeters and sorbent sample tubes are given in Table 1. A representative chromatographic program is shown in Figure 8 for a standard detection by the Hall electrolytic conductivity detector (HECD). The GC column effluent is split and sent to both a Hall electrolytic conductivity detector and a photoionization detector (PID) for selective determination of halogens and semi-selective determination of aromatics, respectively (Figure 9).

TABLE 1. GAS CHROMATOGRAPH/HALL ELECTROLYTIC CONDUCTIVITY DETECTOR CONDITIONS FOR DOSIMETER ANALYSES

Instrument:	Chromatograph:	Hewlett-Packard Model 5711
	Hall Detector:	Tracor Model 700 (in chlorine mode)
	Auto Sampler:	Hewlett-Packard Model 7671-A

Column: 2.44 m x 2 mm (ID) glass packed with 1% SP1000 on 60/80 mesh Carbopack B

Temperature Program: 60°C to 210°C at 8°C/min, hold at 210°C for 15 min

Other Conditions:

Parameter	Temperature, °C
Injection Port	200
Transfer Line	250
Hall Reactor	850
	Flow rate, mL/min
Helium (carrier)	40
Hydrogen (reactor gas)	45
Electrolyte (n-propanol)	0.75

Figures 10 through 12 demonstrate the performance of the chromatographic system in the analysis of complex mixtures of a wide variety of halogenated hydrocarbons.

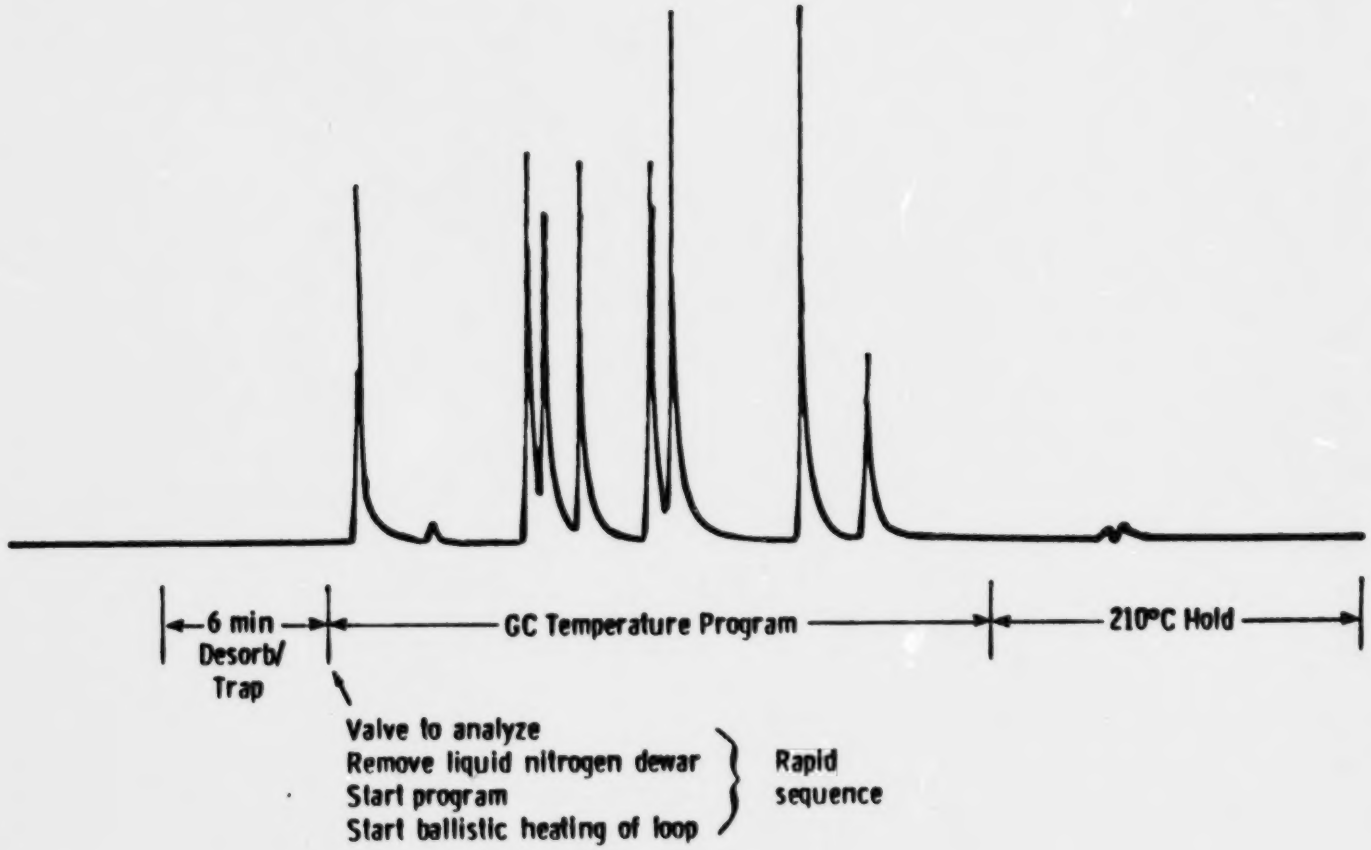


Figure 8. Representative chromatographic program.

Reproduced from
best available copy.

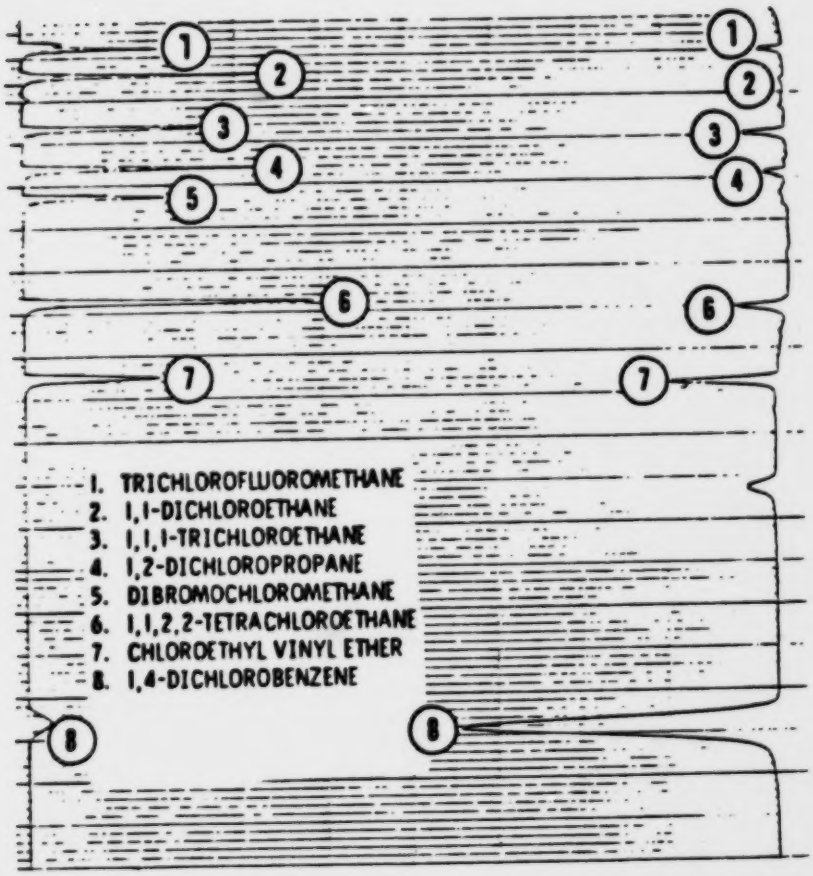


Figure 9. Compound specificity enhancement by use of multiple GC detectors.

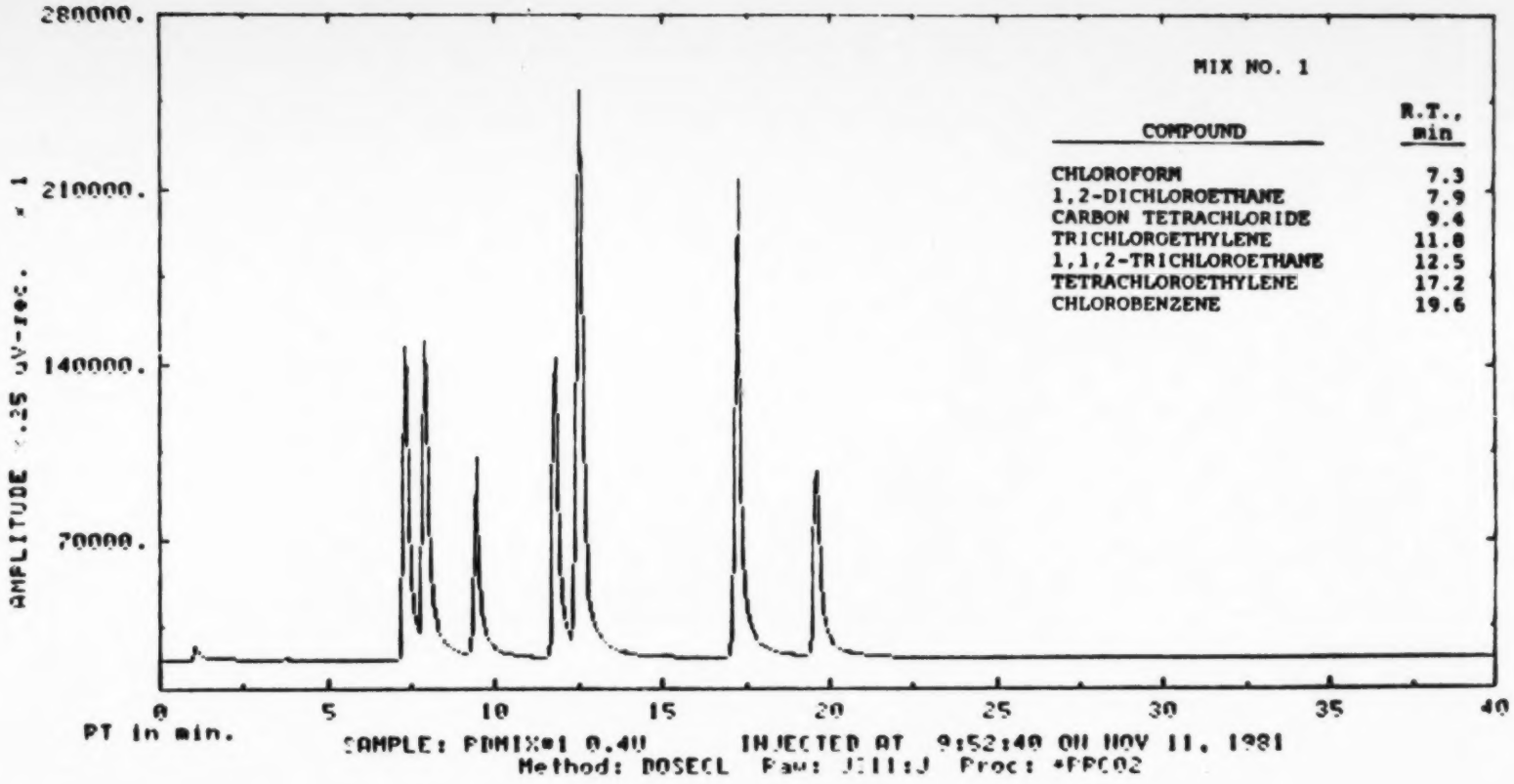
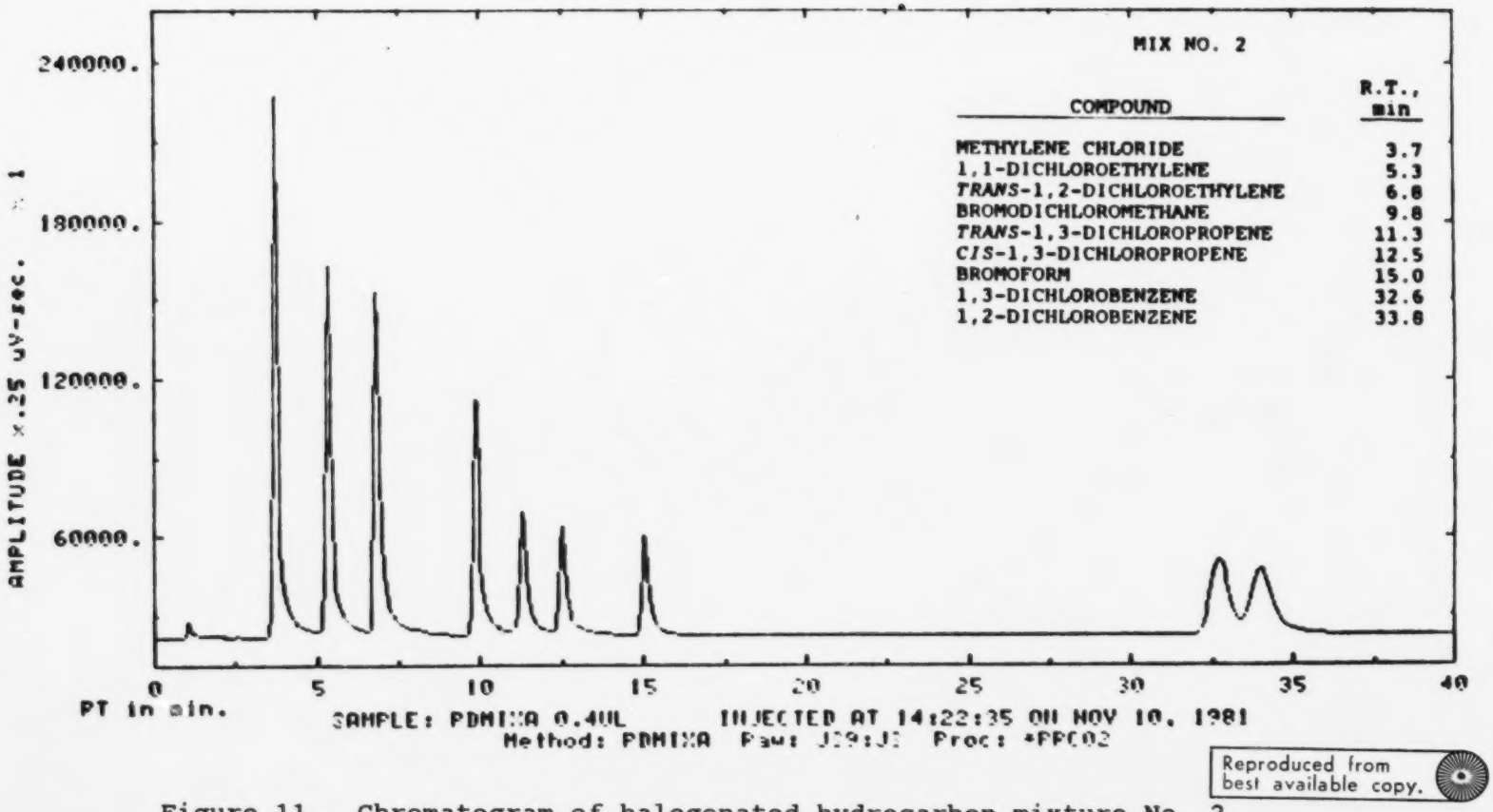


Figure 10. Chromatogram of halogenated hydrocarbon mixture No. 1.



Reproduced from best available copy.

Figure 11. Chromatogram of halogenated hydrocarbon mixture No. 2.

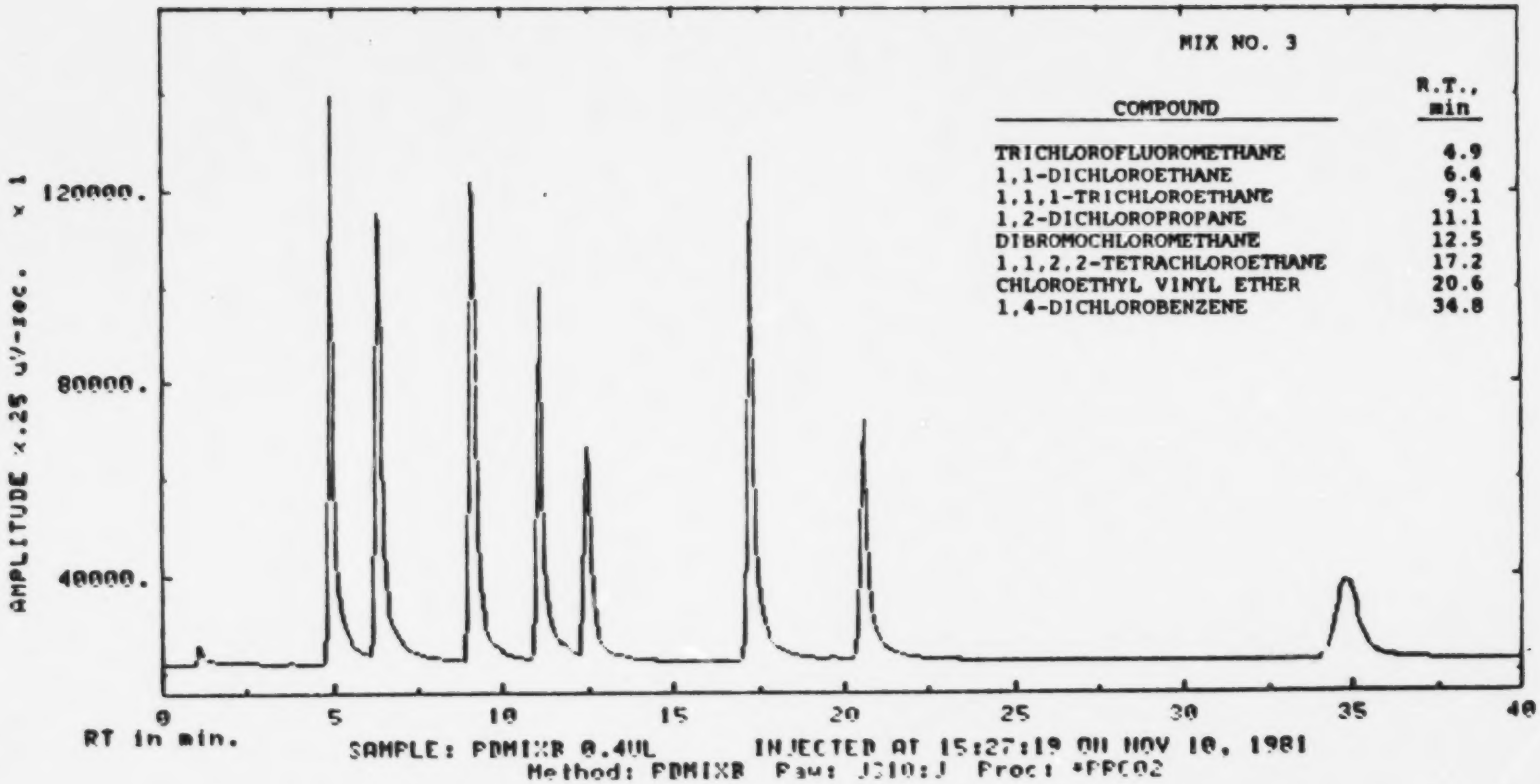


Figure 12. Chromatogram of halogenated hydrocarbon mixture No. 3.

SECTION 3

EXPERIMENTAL

EXPERIMENTAL TEST FACILITIES

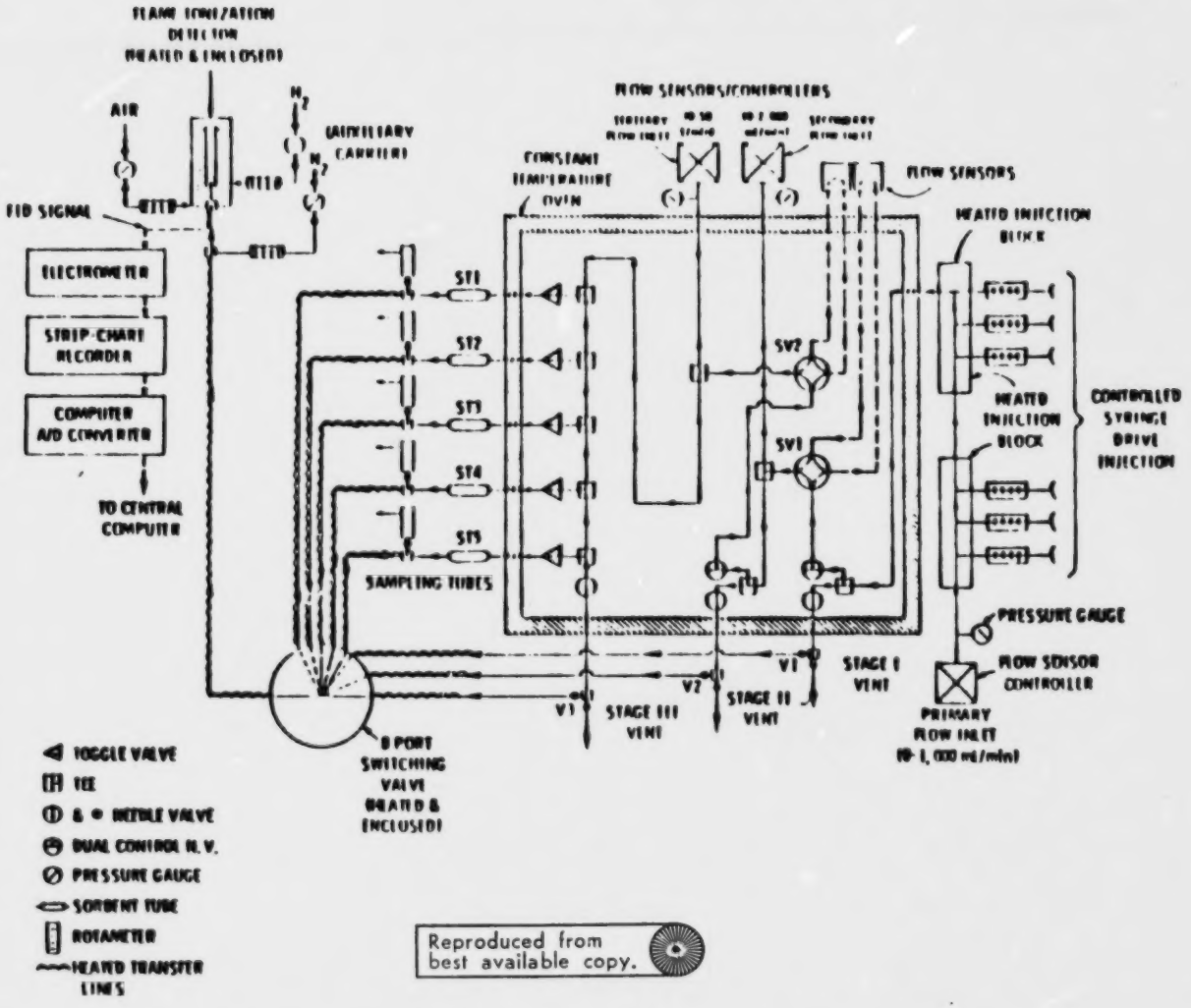
Standards Generation System

Standards for this program were prepared by successive dilutions of stock solution. Stock solutions were prepared using either gravimetric or volumetric addition of the solute to a small portion of the solvent, followed by dilution to volume. In addition to liquid standards, gas standards were generated for dosimeter evaluation studies using a sample generation system employing a syringe drive of fluids into heated blocks with three calibrated dilution stages.

The sample generation system, shown schematically in Figure 13, included the main frame, which was a modified gas chromatograph with its protective metal covering and detector removed. The oven (30 cm x 30 cm) was located on the left side of the main frame. Of the four heated zones available on the original GC, one controlled the oven temperature, two were used to separately control the temperature of the two three-port injection blocks, and the final zone was available for heating transfer lines used for direct interfacing with a detector in frontal analysis capacity studies. A pyrometer (Simpson 0-500°C), a selection switch, thermocouples, and necessary circuit modifications allowed the monitoring of temperatures in the four zones.

An aluminum plate (45.7 cm x 46.4 cm x 0.6 cm) was attached to the main frame to the right of the oven to accommodate the syringe drives. Necessary bulk head gauges and rotameters were used in the configuration indicated in the figure. Materials of construction for the flow system were either stainless steel or nickel, and the entire system was contained in a large exhaust hood (2.4 m x 1.2 m x 1.5 m) with front and rear access through double sliding doors. Flow control/sensing instrumentation, pressure gauges, and rotameters were mounted on a panel and rack assembly in the hood above the generation system.

The generation system functioned in the following manner. A source of carrier gas (N_2) was introduced into the system and split into primary, secondary, and tertiary flows. The primary flow passed through a mass-flow sensor/controller (Brooks Model 5841) which



Reproduced from best available copy.

Figure 13. Standard Sample Generation System (SGS) with effluent monitor modification.

maintained the flow rate at a preset value (0 t0 1,000 mL/min). This flow passed through individually heated and controlled injection blocks which were each designed to accept three syringes mounted on variable-control syringe drives (Sage Model 355). This permitted the simultaneous introduction of six pure liquid components, or potentially many more, if mixtures of compounds were used in the syringes. The rate of injection could be varied from submicroliter/hour to milliliter/minute by the appropriate choice of syringe size and drive rate. Liquid samples were vaporized in the injection blocks and swept with the carrier gas into a constant temperature oven.

Most of the primary flow passed through the oven and through a needle valve used to regulate the pressure in the primary flow path. It was then expelled to the vent (V1). A small portion (usually 10 mL/min) of the primary flow was removed through a dual-control needle valve and passed into a switching valve (SV1) which was actually one-half of an eight-port switching valve. The second half of the switching valve was used for an identical function in the second dilution stage. The switching valve made it possible to insert a mass-flow sensor (Brooks Model 5810, 0 to 100 mL/min) in the flow path (indicated by the dashed line in Figure 13) to measure the exact split of the primary flow. Once the split had been established, the flow sensor was switched out of the system so that the sensing elements were not subjected to sample-containing organic vapors. The split was maintained by carefully controlling the pressures in each dilution stage.

Pressures were monitored with precision pressure gauges [Heise Model CM, 0 to 6.9 x 10^5 Pa (0 to 100 psi)]. By maintaining a constant pressure in each dilution stage, a constant pressure differential was established between the stages, assuring a consistent split ratio across the needle valves.

The split out portion of the primary flow passed from the switching valve and was combined with the secondary carrier flow which entered the constant temperature oven through a mass-flow sensor/controller (Brooks Model 4841, 0 to 2,000 mL/min). As in the case of the primary flow, most of the secondary flow passed through the oven and was expelled to the vent (V2) through a needle valve. A small portion (usually 10 mL/min) of the secondary flow was removed through a dual-control needle valve and passed into a switching valve (SV2). This valve functioned in an identical manner to SV1 and placed a second mass-flow sensor (Brooks, Model 5810, 0 to 100 mL/min) in the path for measuring the second split.

The split out portion of the secondary flow passed from the switching valve and was combined with the final (tertiary) dilution stream which entered the constant temperature oven through a mass-flow sensor/controller (Brooks Model 5841, 0 to 50 L/min). This final concentration was available for sampling through a five-port manifold system that would accommodate sorbent sampling

tubes. Sampling rates through the sorbent tubes were maintained by rotameters (Brooks Model 1110) at the tube exits. The unused portion from the final dilution stage was expelled to the vent (V3).

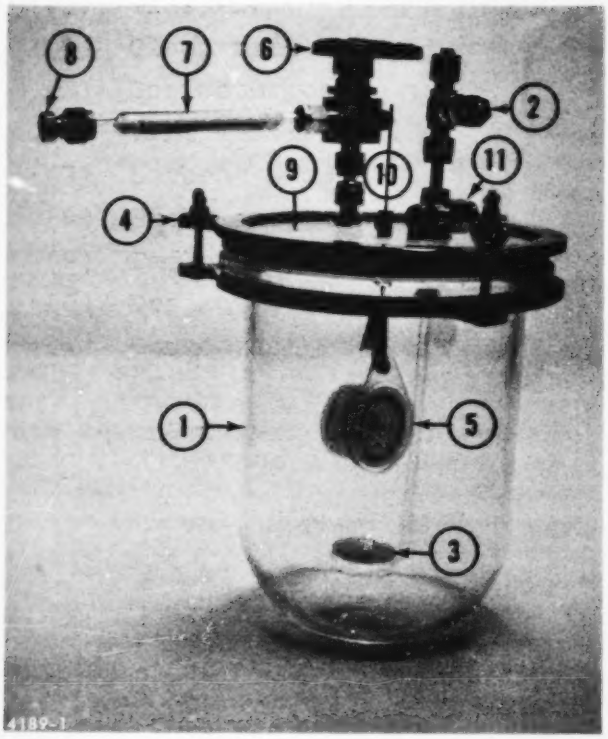
The sample generation system was connected through an eight-port (Valco) selection valve and stainless-steel tubing (1.6 mm) to a flame ionization detector. This arrangement permitted the selective monitoring of concentration levels in each of the three dilution stages and the additional monitoring of effluent from five sampling locations.

Evaluation studies have demonstrated linear concentration responses over the operational ranges of the syringe drive rate, the two split monitors, and the three dilution stages. By the appropriate selection of syringe size, drive rate, split ratios, and dilution rates, it is possible to achieve continuously variable concentrations from percent to low part-per-trillion levels using this system.

Laboratory Test Exposure Chamber

The sampling device was exposed to generated gas mixtures and the concentration of the mixtures was validated by a grab sample or sorbent tube ("active" sampling) sample. A laboratory test exposure chamber, shown in Figure 14 was used. The chamber, designed and assembled to provide test conditions for a previous dosimeter testing and evaluation program, consisted of a 2-liter Pyrex reaction kettle fitted with an "O"-ring-sealed Teflon lid. A standard clamp ring served to seal the lid to the Pyrex vessel. Three ports were provided through the chamber lid. One port was used to admit test gas mixtures into the chamber. Gas line connections were made through appropriate Swagelok® fittings. The gas inlet line terminated into a coarse glass frit which promoted a more even gas flow distribution within the chamber, thus minimizing channeling effects. A second port provided an access for inserting probes into the exposure chamber for monitoring temperature and humidity within the chamber during test runs. Environmental conditions, such as temperature and humidity, could be selected and maintained over a broad range, thus providing means for evaluating dosimeter performance with respect to given environmental parameters.

The third port of the system was fitted with a three-way ball valve which could direct the gas effluent from the exposure chamber to either a vent or sample position. Sorbent tubes were used to collect known volumes of sample in order to validate gas constituent concentration(s) within the chamber during the test. Dosimeters under test were suspended above the glass frit during the exposure period. The distance between the dosimeter and gas entrance could be selected and maintained constant.



(1) Pyrex exposure chamber
(2) Gas inlet fitting
(3) Glass frit
(4) Clamp ring
(5) Dosimeter under test
(6) Vent - sample selection valve
(7) Sorbent sample tube
(8) Probe inlet
(9) Teflon lid
(10) Dosimeter hanger
(11) Connection to sample pump

Figure 14. Exposure chamber for dosimeter testing and evaluation.

Environmental Test Chamber

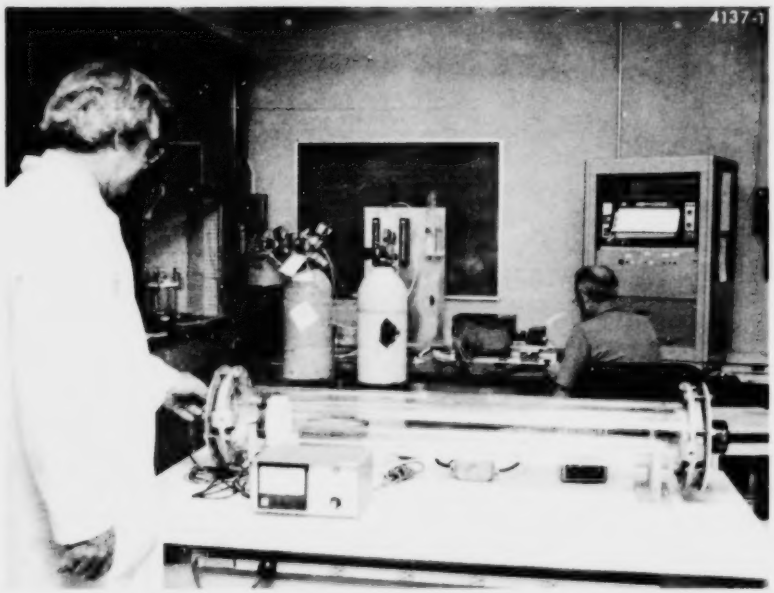
Another means of exposing dosimeters to standard gas concentrations was based on the use of environmental test chamber designed and fabricated at MRC for an ambient air passive dosimeter development program. This facility provided the means by which dosimeters could be subjected to a range of temperatures, humidities, and flow velocities, all of which could be controlled and measured. The test chamber is shown in Figure 15.

The test chamber was fabricated from thick-walled, flanged Pyrex pipe. In this design, a concentric tube arrangement was used. The gas was made to flow down the center tube, back through the space separating the two tubes, then down the center tube again. A variable speed fan was used to circulate the air, and the flow velocity was controlled by adjusting the fan speed. The unit could be operated under stagnant conditions, or could provide high flow regimes. The flanged ends of the chamber were provided with appropriate fittings to admit gases as well as measuring and sampling probes into the system. Gas flows were regulated, measured, and conditioned prior to entry into the chamber. The entire chamber could be heated or cooled. Humidity, likewise, could be controlled and continuously monitored. The system was completely instrumented to monitor environmental conditions within the chamber at all times.

SORBENT SELECTION

While multi-sorbent sampling tubes were employed in the portable miniature sampler to monitor a broad spectrum of environmental contaminants, a single sorbent would be more appropriate for this program because more restrictive sampling was required and sampling would be accomplished by active and passive sampling means. Two sorbents were investigated (Tenax GC and Porapak R) for possible application to Public Health Initiative compounds. Previous success with Porapak R in both active and passive sampling modes prompted the selection of this sorbent for initial testing. Porapak R gives acceptably high breakthrough volumes for the compounds of interest, good absorption/recovery efficiency, and a reasonably clean background on thermal desorption.

The Porapak R sorbent was subjected to a preliminary evaluation to determine its possible application to passive sampling at the 1-ppb level on contract No. 68-02-3469. Porapak R showed promise as a candidate sorbent for this program, based on studies involving relatively high concentrations and solvent extraction procedures. Laboratory studies indicated that high sample recoveries were achieved under direct sample spiking experiments as well as with gas sample exposures.



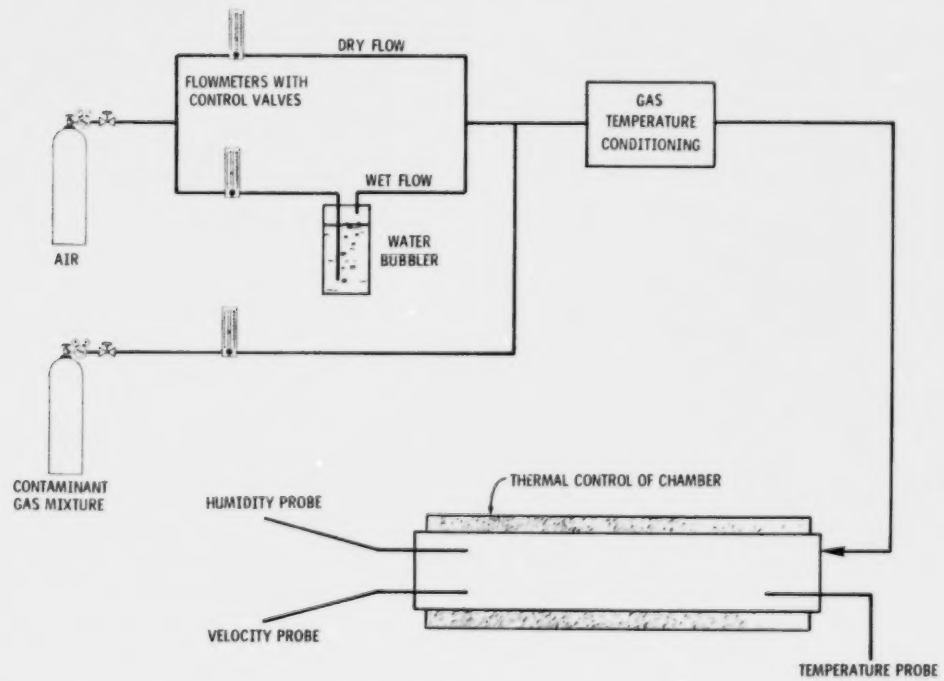


Figure 15. Environmental test chambers for exposure of monitors to selected gases and vapors.

Results obtained with Porapak R elements at the 1-ppb level demonstrated the capability of monitoring at this level under ambient air conditions. Unfortunately, recovery efficiencies at the low concentration levels were considerably lower (40 to 50%) than those achieved with spiked samples. Recovery of chlorobenzene was particularly poor and in many cases uncertain. The performance of the Porapak R elements seemed to decrease with increased use; this was due primarily to the high desorption temperature (~190°C) required, which undoubtedly led to sorbent degradation.

In an effort to improve performance, sorbent elements were prepared using Tenax GC porous polymer. Exposure studies with these elements were much more encouraging leading to recovery efficiencies for all components in excess of 93 percent. One-hour exposures of these elements to the seven-component test gas at the 1-ppb level gave excellent results and indicated that Tenax was the better choice of sorbent.

DOSIMETER TEST RESULTS

Laboratory tests conducted under EPA Contract No. 68-02-3469 comparing dosimeter and active sorbent tubes show good correlation for parallel samples. Tests were performed in the controlled concentration and conditions of the test chambers. Results for a typical test are summarized in Table 2. Other single and dual-face tests under variable time and concentration conditions showed dosimeter to tube ratios varying 0.65 to 1.43 and averaging 1.05 ± 0.2.

TABLE 2. DOSIMETER TEST RESULTS - SINGLE FACE ONE HOUR SAMPLING

Compound	Concentration, ppb		Percent recovery	Concentration, ppb	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
1. Chloroform	11.6	11.1	96	12.9	1.17
2. 1,2-Dichloroethane	13.7	13.7	100	13.8	1.00
3. Carbon tetrachloride	8.8	10.6	120	9.7	0.91
4. Trichloroethylene	10.4	10.2	98	12.1	1.19
5. 1,1,2-Trichloroethane	10.2	11.1	109	12.5	1.13
6. Tetrachloroethylene	8.2	8.6	105	13.7	1.59
7. Chlorobenzene	12.1	11.0	91	12.4	1.13

SECTION 4

EFFECTS OF ENVIRONMENTAL FACTORS

A laboratory investigation was conducted to determine the effects of "environmental factors," such as UV radiation, water vapor, NO_x, and ozone, on the chemical integrity of the compounds of interest. To accomplish this, a method was designed to enable identification and quantitation of the gaseous organic reactants employing packed column/chlorine-specific detector chromatography. Capillary column GC/MS was determined to be the method of choice to detect and identify products resulting from photodegradation, chemical reactions, etc. Environmental effects were studied in two phases. In the first phase, gas phase reactions were studied using Teflon gas bags. Gas samples were extracted from the bag with a gas syringe after exposure and analyzed by GC and/or GC/MS to determine environmental effects. The second phase involved delineating the effects of "environmental factors" on the test compounds sorbed onto a solid sorbent. In this case, the spiked sorbent tube was challenged with UV radiation and/or other chemical species for given periods of time and then thermally desorbed to determine the effects of the exposure. Comparisons were then made with unchallenged spiked tubes used as controls.

GAS BAG EXPERIMENTS PHI COMPOUNDS

Work in this phase of the program was directed toward delineating the effect of UV radiation and other atmospheric contaminants on the chemical integrity of the compounds of interest. Various mixtures of chloroform, 1,2-dichloroethane, carbon tetrachloride, trichloroethylene, 1,1,2-trichloroethane, tetrachloroethylene, and chlorobenzene were prepared by direct injection of liquid standards into a 25-L Teflon gas bag, allowing the liquid to volatilize. The gas bags were fitted with two valves to aid in flushing and/or sample introduction, and with rubber septa for injection of standards into the bag and removal of gas samples by a gas syringe. After gas standards were prepared, the bag was photoexcited for a known length of time using UV light generated in a light box. The bag to be photoexcited was hung in the UV light box as shown in Figure 16. The two sets of lights were turned on and allowed to photoexcite the sample gases. Analyses were run at predetermined times on both the control and the photoexcited gags. A control sample was maintained in a light-protected environment to separate the effect of temporal degradation from photodegradation. After exposure, the contents of both bags were analyzed by packed column

GC. In cases where some dramatic effect was observed, samples also were analyzed by GC/MS. All GC/MS peaks reconstructed by the computer that were greater than 10 percent above background were identified. Relative quantities of materials produced or destroyed were determined by comparing the areas of the major ions from their mass spectra.

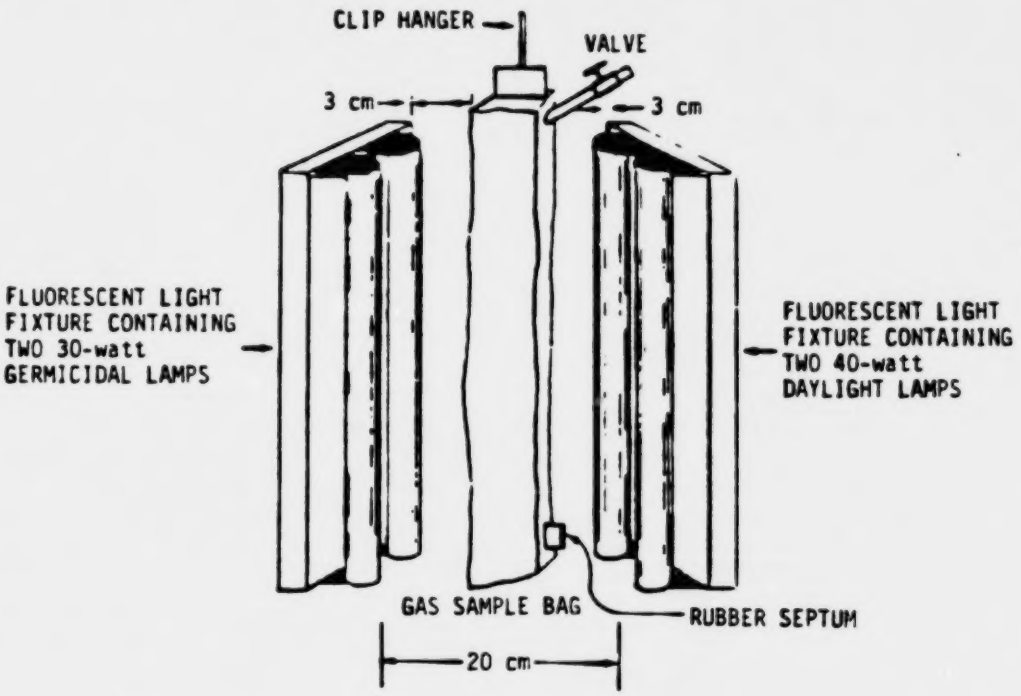


Figure 16. UV light box used for photoexcitation.

A UV-Vis absorption spectrum of the Teflon bag material was obtained to determine UV-Vis absorption characteristics of the bags through which the light for the photoexcitation must pass. The Teflon bags do not absorb light in the UV-Vis spectrum until ~300 nm. A 50 percent absorption occurs at 215 nm (Figure 17). Tedlar bags also were used in these studies but absorption occurred in the UV. Consequently, longer exposures were required to show compound degradation.

In an earlier experiment studying the photodegradation products of chlorinated organics, it was found that 1-hour exposure in the light box in Figure 16 gave similar results to 3 days exposure in the Sunlighter II Lightbox (Text-Lab Apparatus Co., Amhurst, NH). One-day exposure in the Sunlighter II is equal to 0.3 year

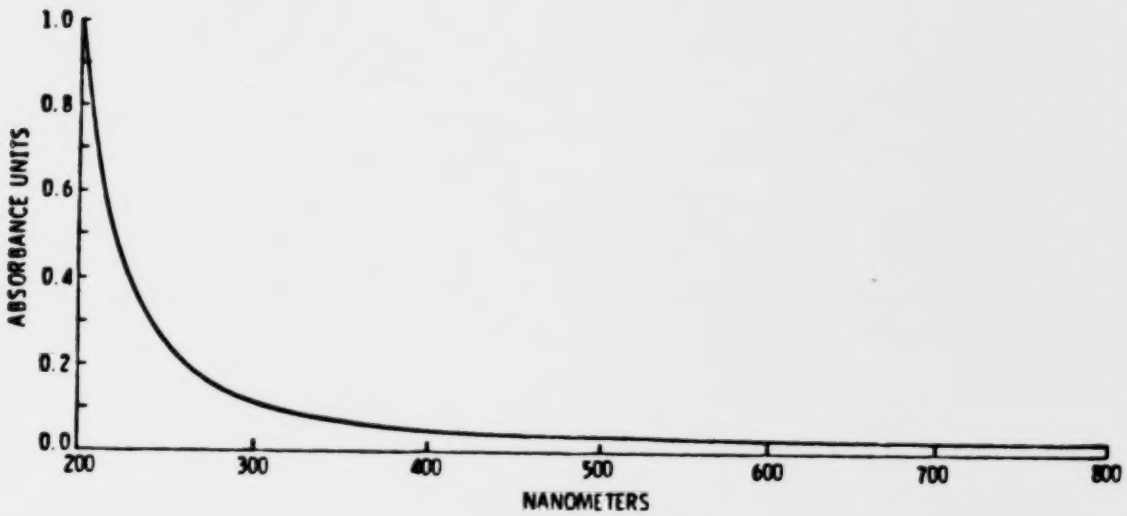


Figure 17. UV-Vis absorption spectrum of Teflon sample bag.

of natural sunlight (average yearly sunlight for Denver or south Florida). Therefore, a 1-hour exposure in the light box is approximately equal to one year of exposure to natural sunlight.

Gas samples were made up in nitrogen, ambient air, and water-saturated air matrices, and compound stability was determined as a function of matrix and time as well as UV exposure. Little change in compound concentration was observed over long periods of time in nitrogen, ambient-air, or water-saturated air matrices. Exposure to UV radiation caused dramatric reductions in concentration for the ethanes and ethylenes in the Teflon gas bags. Similar reductions were noted for Tedlar bags, but they were not as extensive due to the greater absorption of UV radiation by Tedlar. Results of these studies are summarized in Tables 3 and 4. GC/MS analysis were conducted on samples showing excessive degradation in the hope of identifying new compounds that may have been formed. Such analyses substantiated work done on packed column GC but did not identify any new compounds.

Similar runs were conducted to determine the effects of ozone on a mixture of the PHI compounds. In this study, gas mixtures were prepared as before in 25-liter gas bags. Samples were extracted with a gas syringe and analyzed by GC and/or GC/MS. The diluent gas in this case contained either 1 ppm or 10 ppm of ozone. Ozone was generated using a Model 50G-1 stable ozone generator (Ultra-Violet Products, Inc., San Gabriel, CA, 91778). Results of this study are given in Table 5. As is apparent from the tabulated data, no meaningful effect was produced by ozone on the chemical integrity of the gas mixture under study.

TABLE 3. PERCENT RECOVERY VS EXPOSURE TO UV RADIATION

Compound[a]	Light box exposure		Exposure to Sunlighter		
	1 hr	2 hr	1 hr	3 hr	72 hr
Chloroform	110	14	102	97	87
1,2-Dichloroethane	100	5	103	95	79
Carbon tetrachloride	108	69	103	93	88
Trichloroethylene	10	5	99	87	36
1,1,2-Trichloroethane	84	4	107	93	75
Tetrachloroethylene	5	<1	112	98	56
Chlorobenzene	10	3	113	95	41

[a]Gas mixture contained in Teflon bag (nitrogen matrix).
Sample size = 5 mL.

TABLE 4. PERCENT RECOVERY ON EXPOSURE IN LIGHT BOX

Compound[a]	Analyzed same day							Analyzed 24 hr later	
	15 min.		45 min.		N_2	1 hr, 45 min.			
	1[b]	2[c]	1[b]	2[c]	60 min.	1[b]	2[c]	1[b]	2[c]
Chloroform	99	96	104	90	90	106	92	115	102
1,2-Dichloroethane	99	96	107	91	88	106	90	114	101
Trichloroethylene	95	94	104	88	87	103	90	117	98
1,1,2-Trichloroethane	94	93	94	85	81	83	77	76	73
Tetrachlorethylene	95	91	98	81	77	80	69	72	59
Chlorobenzene	91	89	94	83	83	84	72	89	66

[a]Gas mixture contained in Tedlar bag; 5-mL sample size.
[b]Air matrix.
[c]Air saturated H_2O matrix.

TABLE 5. OZONE EXPOSURE STUDIES

Compound	RT,[a] min.	Control (zero air) Initial	Control (zero air) 24 hr	1-ppm O_3 exposure[b] Initial	1-ppm O_3 exposure[b] 24 hr	10-ppm O_3 exposure Initial	10-ppm O_3 exposure 24 hr
Methylene chloride	3.71	7.6	7.6	10.1	9.0	8.1	8.1
Chloroform	7.31	167	163	272	258	173	155
1,2-Dichloroethane	7.90	178	167	286	266	173	158
1,1,2-Trichloroethane	9.09	11.4	14.5	-	217	11	11
Carbon tetrachloride	9.44	244	243	404	405	256	225
Trichloroethylene	11.78	201	195	343	309	206	184
1,1,2-Trichloroethane	12.50	241	235	403	359	234	223
Tetrachloroethylene	17.2	247	238	407	373	252	229
Chlorobenzene	19.59	251	235	417	369	222	211

[a] RT = retention time.

[b] Smaller dilution factor = higher concentration than control.

GAS BAG EXPERIMENTS WITH COMPLEX GAS MIXTURE

Concurrent with the work involving chlorinated organics, studies were conducted on a more complex gas mixture to determine UV effects on composition. In this study, internal combustion engine exhaust products were collected and expoed to UV radiation. Identification of gaseous organic reactants and products from photodegradation at levels above 10 ppm in the exhaust were determined by capillar column GC/MS.

The exhaust gases were trapped in a Teflon bag. Capillary-GC/MS analyses were performed on the exhaust. The bag was photoexcited for a known length of time using UV light generated in the light box. A control sample was maintained in a light-protected environment to separate the effect of temporal degradation from photo-induced degradation. After exposure, the contents of both bags were analyzed. All GC/MS peaks reconstructed by the computer that were greater than 10 percent above background were identified. Relative quantities of material produced or destroyed were determined by comparing the areas of the major ion peaks from their mass spectra.

The exhaust gases, both photoexcited and nonphotoexcited, were analyzed directly by GC/MS with a capillary column under the following conditions.

- HP-5982 GC/MS
- Nutech thermal desorption system
- 25-m, WCOT fused silica capillary column coated with SE-54
- Initial temperature at 40°C
- Hold for 5 min at 40°C
- Heat at 8°C/min
- Final temperature at 250°C
- MS operated in scanning mode between 35 amu to 500 amu/ 1 second
- He carrier gas
- Injection of 5 mL of gases from bag.

Procedure

Five milliliters of exhaust gases (either photoexcited or non-excited) were injected into the Nutech thermal desorption system (Figure 18), which was modified by replacement of the desorption chamber, used for samples on packed tubes such as Tenax, with a rubber septum. This allowed injection of gases directly by the use of a gas syringe. The gases were trapped in the micro trap at -70°C (cooled with liquid N_2). After trapping, the valve was changed to "inject" and the trap heated to 250°C in 2 minutes. The vapors were then flashed into the capillary GC and analyzed by the mass spectrometer. Both bags were analyzed each time to separate the effect of temporal degradations from photoinduced degradation.

The compounds separated by the GC and detected by the MS were identified by comparisons of the generated mass spectra to known spectra by the use of the Eight Peak Index of Mass Spectra (Vol 1, 2, 3, 4, second edition 1974, Mass Spectrometry Data Centre, AWRE, Aldermaston, United Kingdom). All identifications were tentative until the same compounds were run under conditions of this experiment.

The relative concentration changes of the compounds over the experimental period were determined by the areas of the major m/z peak for each compound and compared over the times, because all GC/MS runs were under similar MS conditions. No absolute quantitation was accomplished because standards of all compounds found would have had to be run under similar conditions.

Results

The results are reported below as compounds detected. The relative changes in these compounds are given based on the unexposed sample. The compounds were grouped together in similar chemical classes where possible. Examples of these groupings are: benzene, C_1-benzenes, C_2-benzenes, C_3-benzenes, and aliphatics.

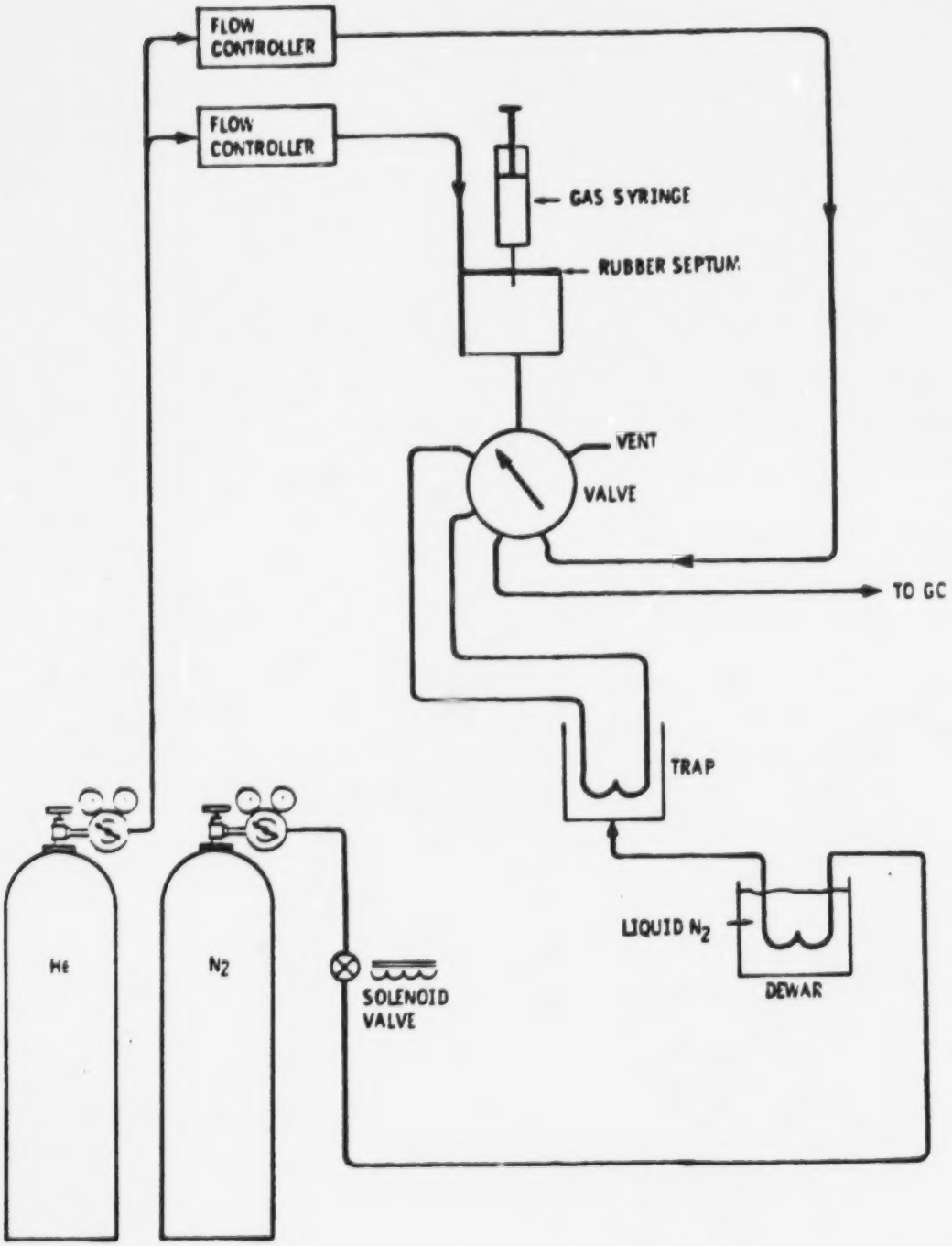


Figure 18. Flow diagram for Model 320 modified thermal desorption system.

The unexposed sample did not change substantially from the time of sampling up to 72 hours in the dark. Only slight losses were seen, which could be due to absorption of vapors by the bag. This is shown in Table 6. The relative percent change after exposure to UV light is given in Table 7. The relative amounts in the unexposed sample is given in Table 8. Table 9 gives the actual compounds found, their retention times, and the experiments in which they were found as distinct GC/MS peaks. The aliphatic hydrocarbons found in the 16-hour exposure experiment and not in the 0-hour or 1-hour exposure experiments are not to be considered as photooxidation products. These peaks also were in the other experiments but were masked due to the large aromatic peaks detected in the 0-hour and 1-hour experiments that are absent in the 16-hour experiment.

A comparison of the GC/MS traces for the unexpoed, 1-hour UV exposure, and 16-hour UV exposure are given in Figure 19. Apparent peaks in the 16-hour exposure are generally due to background noise and are the result of the computerized normalization process for the very small real peaks that are present in the sample.

SOLID SORBENT STUDIES

A series of experiments was conducted to determine if the chemical integrity of the PHI compounds sorbed onto a porous polymer could be challenged by environmental factors as in the gas bag studies. This case represents the sampling context for the compounds of interest and, consequently, sample integrity is paramount to the sampling scheme. Tenax GC was used to charge the active sampling tubes. Sorbed compounds were thermally desorbed and analyzed by GC and/or GC/MS. Preliminary results indicated no significant change in sample composition when spiked sorbent tubes were challenged with water vapor or the acid vapors commonly expected in the ambient air environment. Acid vapors can adversely affect sampling efficiency, however, by chemical degradation of the porous polymer rather than artifact formation involving the sorbed sample.

Rather dramatic changes were caused by UV radiation in the gas bag studies. Similar studies were conducted in this phase of the program to ascertain if parallel results could be obtained when the same compounds were sorbed onto Tenax GC. In this case, spiked tubes were exposed to strong UV radiation for 2 hours and analyzed. These results were compared to unradiated spiked tubes. Results are given in Table 10. No change in sample composition was noted. In addition to the UV experiments, spiked tubes were exposed to two levels of ozone employing the Model 506-1 ozone generator used earlier. The experimental arrangement is shown in Figure 20. Details and results of this study are given in Table 11. Again, no significant difference was seen between exposed and unexposed sampling tubes.

TABLE 6. UNEXPOSED SAMPLE PERCENT CHANGE IN COMPOSITION

Compound or class	Time after sampling				
	0 hr	4 hr	24 hr	48 hr	72 hr
Benzene	0	-5%	-5%	-6%	-3%
Toluene	0	-2%	-2%	-1%	-2%
Xylenes	0	-2%	-2%	-5%	-5%
C_3-Alkyl benzene	0	-7%	-9%	-9%	-10%
C_4-Alkyl benzenes	0	-7%	-10%	-6%	-8%
C_9-C_{15} Aliphatics	0	-1%	0	-1%	-1%
Tolualdehyde	0	-5%	-10%	-10%	-7%
Acetic acid	0	-10%	-10%	-11%	-11%
Methyl styrene	0	-10%	-10%	-15%	-10%
Ethyl styrene	0	-10%	-7%	-12%	-10%
Methyl phenyl acetylene	0	-2%	-5%	-8%	-10%
Ethyl benzyl ether	0	-2%	-2%	-5%	-2%
Naphthalene	0	-1%	-7%	-1%	-0%
Methyl naphthalene	0	-1%	0%	-5%	0%
C_2-Alkyl benzaldehyde	0	-10%	-10%	-6%	-12%

TABLE 7. PERCENT CHANGE IN COMPOSITION UPON EXPOSURE TO UV RADIATION

Compound or class	Time after exposure		
	0 hr	1 hr	16 hr
Benzene	0	-1%	-30%
Toluene	0	-5%	-60%
Xylenes	0	-50%	-99%
C_3-Alkyl benzene	0	-40%	-99%
C_4-Alkyl benzenes	0	-60%	-98%
C_9-C_{15} Aliphatics	0	0%	-10%
Tolualdehyde	0	-10%	-95%
Acetic acid	0	-5%	-50%
Methyl styrene	0	-50%	-90%
Ethyl styrene	0	-50%	-80%
Methyl phenyl acetylene	0	-60%	-70%
Ethyl benzyl ether	0	-10%	-75%
Naphthalene	0	-15%	-20%
Methyl naphthalene	0	-20%	-90%
C_2-Alkyl benzaldehyde	0	-30%	-90%

TABLE 8. RELATIVE AMOUNTS IN THE UNEXPOSED SAMPLE

Compound or class	Relative amounts in the unexposed sample
Benzene	10
Toluene	10
Xylenes	100
C_3-Alkyl benzenes	40
C_4-Alkyl benzenes	4
C_9-C_{15} Aliphatics	10
Tolualdehyde	1
Acetic acid	2
Methyl styrene	1
Ethyl styrene	0.4
Methyl phenyl acetylene	0.1
Ethyl benzyl ether	2
Naphthalene	6
Methyl naphthalene	0.5
C_2-Alkyl benzaldehyde	0.3

TABLE 9. COMPOUNDS DETECTED BY MASS SPECTROMETRY AS DISTINCT PEAKS

RT[a]	Compound	Unexposed sample	1-hr UV exposure	16-hr UV exposure
2.5	Carbon dioxide, CO_2	X	X	X
2.8	C_2-Alkyl benzene	X	X	
7.9	Aliphatic			X
8.2	C_2-Alkyl benzene	X	X	
8.6	Aliphatic		X	X
9.6	Tolualdehyde, C_8H_8O	X	X	
9.8	C_3-Alkyl benzene	X	X	
10.0	C_3-Alkyl benzene	X	X	
10.4	C_3-Alkyl benzene	X	X	
10.5	Aliphatic			X
10.6	Acetic acid	X	X	X
10.8	C_3-Alkyl benzene	X	X	
11.0	C_{10}-Aliphatic	X	X	
11.1	C_3-Alkyl benzene	X	X	
11.2	Aliphatic			X
11.4	Methyl styrene, C_9H_{10}	X	X	
11.6	Methyl phenyl acetylene C_9H_8	X		
11.7	C_4-Alkyl benzene	X	X	
11.8	C_4-Alkyl benzene	X	X	
11.9	C_4-Alkyl benzene	X	X	
11.6	C_4-Alkyl benzene	X	X	
12.0	Ethyl benzyl ether	X		
12.0	Aliphatic			X
12.3	C_4-Alkyl benzene	X	X	
12.4	Aliphatic			X
12.4	C_4-Alkyl benzene	X	X	
12.5	Aliphatic			X
12.8	C_4-Alkyl benzene	X	X	
12.8	Aliphatic			X
13.1	C_4-Alkyl benzene	X	X	
13.2	Aliphatic			X
13.3	Ethyl styrene, $C_{10}H_{12}$	X	X	
13.4	Ethyl styrene, $C_{10}H_{12}$	X	X	
14.2	Naphthalene	X	X	X
14.1	C_2-Alkyl benzaldehyde		X	
16.4	Methyl naphthalene	X	X	

[a]RT = retention time.

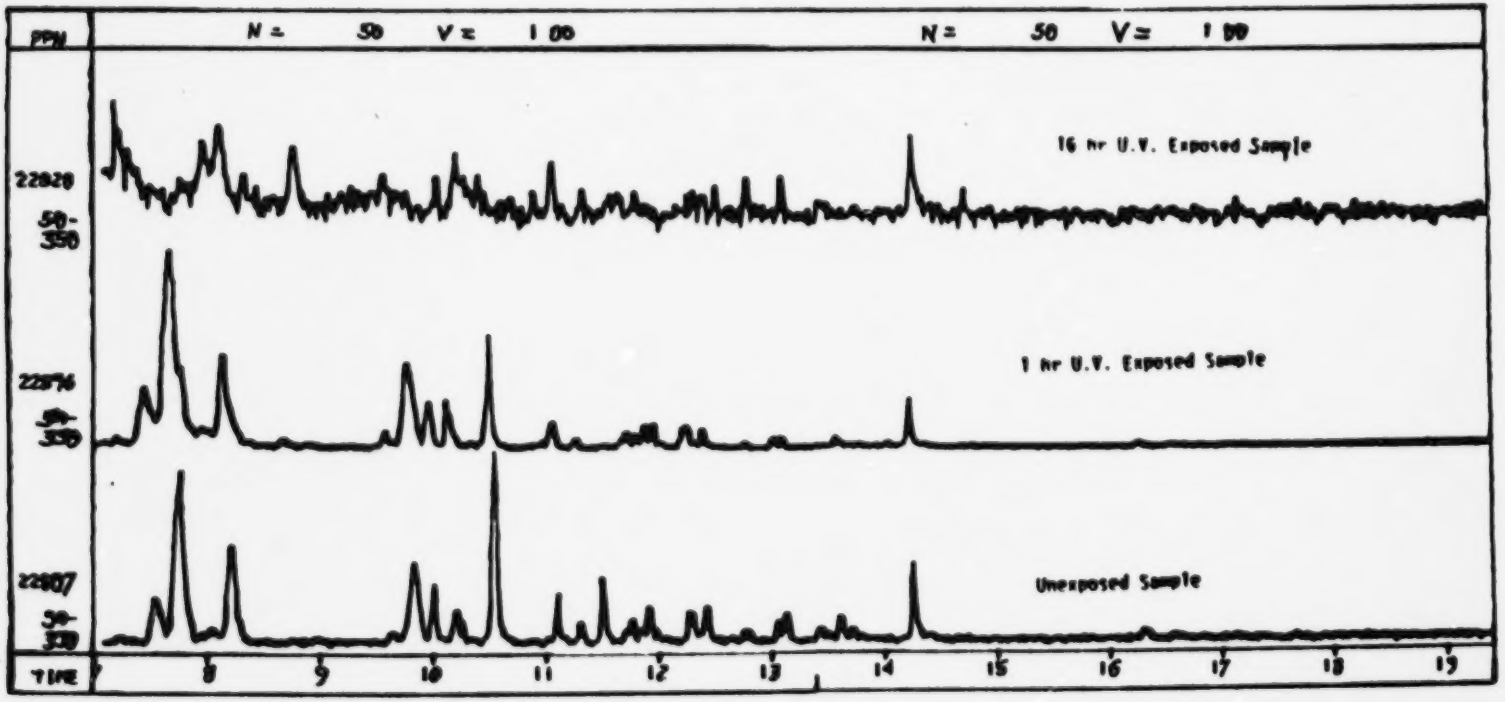


Figure 19. GC/MS traces of the exhaust gases before and after exposure.

TABLE 10. UV RADIATION STUDY OF SPIKED SAMPLING TUBES

Compound	RT,[a] min	Concentration, ng: Spiked tube	Concentration, ng: 2-hr UV
Methylene chloride	3.71	5.7	8.0
Chloroform	7.31	355	348
1,2-Dichloroethane	7.90	409	374
1,1,1-Trichloroethane	9.09	2.7	2.9
Carbon tetrachloride	9.44	436	423
Trichloroethylene	11.78	481	443
1,1,2-Trichloroethane	12.50	507	491
Tetrachloroethylene	17.20	532	565
Chlorobenzene	19.59	549	633

[a]RT = retention time.

TABLE 11. OZONE EXPOSURE OF SPIKED SORBENT TUBES

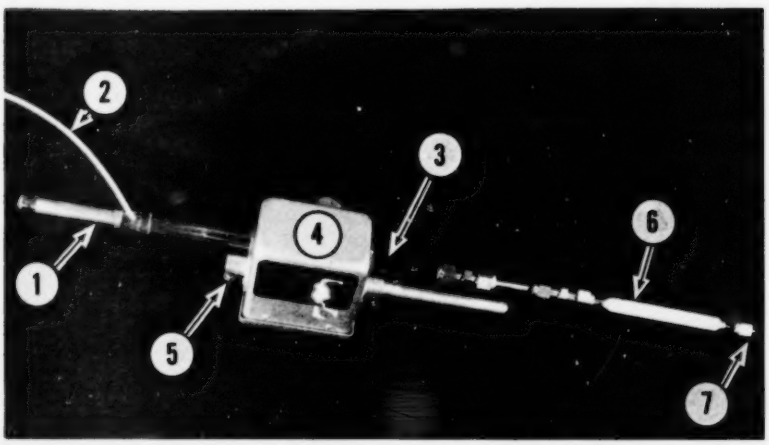
Compound	RT,[a] min	Concentration, ng: Spiked tube[b]	Concentration, ng: 1-ppm O_3[c]	Concentration, ng: 10-ppm O_3[d]
Methylene chloride	3.71	45.2	23.2	34.5
Chloroform	7.31	90.0	103.0	20.0
1,2-Dichloroethane	7.90	88.0	88.0	78.0
1,1,2-Trichloroethane	9.09	88.0	85.0	85.0
Carbon tetrachloride	9.44	105.0	103.0	79.0
Trichloroethylene	11.78	92.0	94.0	89.0
1,1,2-Trichloroethane	12.50	88.0	85.0	85.0
Tetrachloroethylene	17.2	85.0	86.0	86.0
Chlorobenzene	19.59	90.0	91.0	85.0

[a]RT = retention time.

[b]Tenax tube spiked with 1 μL of a 100 μg/μL mixture and purged for 2 hours with air at 50 cc/min.

[c]Same as (b) but purged with 1.0 ppm O_3 for 2 hours at 50 cc/min.

[d]Same as (b) but purged with 10 ppm O_3 for 2.5 hours at 36 cc/min.



(1) Mercury discharge lamp
(2) Air and/or oxygen inlet
(3) Quartz tube
(4) Housing
(5) Lamp position for low-concentration ozone generation
(6) Spiked Tenax-GC sampling tube
(7) Tube outlet to flow control and flowmeter

Figure 20. Ozone generator setup for sorbent tube exposure studies.

SECTION 5

RESULTS AND CONCLUSIONS

As defined in Section 1 the goals of the program included to develop, optimize, and evaluate sampling and analysis procedures for atmospheric monitoring of potentially hazardous organic compounds and evaluate environmental factors on sampling and analysis procedures. The following results and conclusions were determined:

- A passive exposure monitor (PEM) for sampling hazardous organic compounds at low ppb levels including halogenated and aromatic organics was developed by MRC under this and other EPA contracts. Method development information is provided in other contract reports (contract numbers 68-02-3469 and 68-02-3699).

- Evaluation of two sorbent materials, Poropak B and Tenax GC was conducted. Results indicated Tenax GC obtained better recoveries for the compounds of interest.

- Exposure of Teflon gas bags containing various mixtures of chloroform, 1,2-dichloroethane, carbon tetrachloride, trichloroethylene, 1,1,2-trichloroethane, tetrachloroethylene, and chlorobenzene were exposed to UV light for a variety of time periods and analyzed. Little change in compound concentration was observed over long exposure periods of samples in air, water, or nitrogen matrices. Dramatic reduction for the ethanes and ethylenes in the Teflon bags did occur.

- Gas bags samples containing organic compounds in ozone diluent showed no meaningful effect was produced by ozone on the chemical integrity of the gas mixture under study.

- UV light studies of gas bags containing more complex organic matrix obtained from combustion engine exhaust showed extensive change (>50%) to many organic compounds which were at initial concentrations of >10 ppm.

- Two studies involving the effect of UV light and ozone levels on chemical integrity of organic compounds on sorbent polymer tubes shows no significant difference between exposed and unexposed sampling tubes.